Asymmetric Epoxidation of Simple Olefins Catalyzed by Chiral Diphosphine-Modified Platinum(II) Complexes

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The synthesis of a class of chiral diphosphine-modified platinum(II) complexes of the type P_2*Pt(CF_3)X (P_2* = chiraphos, prophos, diop; X = Cl, OH) is reported. These have been characterized with IR and ^{19}F and $^{31}P\{^1H\}$ NMR spectroscopy. The hydroxo complexes and the corresponding [P_2*Pt(CF_3)(CH_2Cl_2)](BF_4) cationic solvato complexes have been used as catalysts in the epoxidation of 1-octene and propene with diluted hydrogen peroxide. The obtained epoxides are optically active with enantiomeric excess (ee) as high as 41%. The capacity of the catalysts to induce asymmetry is discussed on the basis of the stereochemical rigidity of the metal–diphosphine array that has been investigated with variable-temperature ^{19}F NMR experiments.

Introduction

Despite the importance of chiral expoxides in organic synthesis,[2] to date the available chemical routes to the asymmetric epoxidation of simple, unfunctionalized olefins have met with only moderate success,[3-11] the highest ee having been obtained either with microbiological[12,13] or with "bio-type" systems.[14,15] Conversely in the epoxidation of allylic alcohols, Sharpless has reported the use of a very efficient, low cost catalytic system which enables the achievement of considerable asymmetric inductions, often higher than 90%.[16-18] These results underline the importance of the so-called "secondary interaction" in asymmetric catalysis,[19] i.e. the capability of certain functionalized olefinic substrates to bind the metal center on more than one site, thereby ensuring a more efficient facial discrimination in the prochiral carbon–carbon double bond. In the absence of the secondary interaction (i.e. with simple olefins), one can rely only on the structural and conformational rigidity of the metal system as the factor capable of maximizing the free energy difference between the diastereomeric intermediates leading to the asymmetric discrimination. In the case of epoxidation significant results with simple olefins (ee 16–35%) have been obtained stoichiometrically by using Mo(VI) oxo diperoxo complexes modified with (*S*)-*N*,*N*-dimethyllactamide.[4] However, a stoichiometric system differs from a catalytic one in the number of mechanistic steps leading to the regeneration of the active species, which may alter the conformational rigidity of the working catalyst and reduce strongly its capacity to induce asymmetry. This is demonstrated for example by a Mo(VI) system[5] closely related to that reported above, which catalyzes the epoxidation of simple olefins with *t*-BuOOH, where the extent of asymmetric induction is rather poor (ee 1–7% in the majority of cases). Other examples of catalytic epoxidation of simple olefins have been recently reported by Curci et al.[11] with a purely organic system, where the extent of asymmetric induction was only slightly increased (ee 6–12%) and by Groves[14] and Mansuy[15] both using chiral Iron porphyrin complexes as catalysts and iodosyl benzene as the oxidant (ee up to 51%).

The results so far obtained reveal the importance of ligand design in ensuring the appropriate structural and conformational rigidity to the working catalyst. From this point of view the major innovations have been achieved in the field of asymmetric hydrogenation based on rhodium–phosphine systems, where a wide variety of sophisticated chiral diphosphine ligands have been devised,[19] some which have become also commercially available.

We have recently reported the selective epoxidation of terminal olefins with hydrogen peroxide catalyzed by Pt(II) complexes of the type P_2Pt(Rx)X (P_2 = diphosphine ligand; Rx = Ph, CF_3; X = solvent, –OH)[20,21] which allow the chiral diphosphine approach to asymmetric epoxidation. We now wish to report the synthesis and characterization of the chiral diphosphine-modified Pt(II) complexes and their use as catalysts in the asymmetric epoxidation of simple olefins (1-octene, propylene).

Results and Discussion

Synthesis and Characterization of the Chiral Complexes. The chiral diphosphine-modified Pt(II) complexes

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(2) See, for example: Baldwin, J. J.; Raab, A. W.; Mensler, K.; Arison, B. H.; McClure, D. E. *J. Org. Chem.* **1978**, *45*, 4876 and references therein.
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Table I. Spectroscopic Features of the Chiral Pt(II) Complexes[a]

complex	IR	^{19}F NMR	$^{31}P\{^1H\}$ NMR
(chiraphos)Pt(CF_3)Cl	320 m (ν_{Pt-Cl})	−29.44 (dd, $^{o}J_{F-Pcis}$ = 11.9, $^{3}J_{F-Ptrans}$ = 57.5, $^{2}J_{F-Pt}$ = 559)	39.96 (dq (trans CF_3), $^{3}J_{P-F}$ = 57.5, $^{2}J_{P-P}$ = 16.6, $^{1}J_{P-Pt}$ = 1797), 40.76 (dq (cis CF_3), $^{3}J_{P-F}$ = 11.9, $^{2}J_{P-P}$ = 16.6, $^{1}J_{P-Pt}$ = 3890)
(chiraphos)Pt(CF_3)(OH)	3625 m (ν_{O-H})	−29.63 (dd, $^{3}J_{F-Pcis}$ = 8.8, $^{3}J_{F-Ptrans}$ = 54.1, $^{2}J_{F-Pt}$ = 584)	39.17 (dq (trans CF_3), $^{3}J_{P-F}$ = 54.1, $^{2}J_{P-P}$ = 13.8, $^{1}J_{P-Pt}$ = 2028), 34.83 (dq (cis CF_3), $^{3}J_{P-F}$ = 8.8, $^{2}J_{P-P}$ = 13.8, $^{1}J_{P-Pt}$ =3203)
(prophos)Pt(CF_3)Cl	305, 312 m (ν_{Pt-Cl})	−24.34 (dd, $^{3}J_{F-Pcis}$ = 13.0, $^{3}J_{F-Ptrans}$ = 57.0, $^{2}J_{F-Pt}$ = 564), −25.44 (dd, $^{3}J_{F-Pcis}$ = 11.8, $^{3}J_{F-Ptrans}$ = 58.0, $^{2}J_{F-Pt}$ = 559)	[b]
(prophos)Pt(CF_3)(OH)	3628 w (ν_{O-H})	−28.33 (dd, $^{3}J_{F-Pcis}$ = 9.7, $^{3}J_{F-Ptrans}$ = 54.5, $^{2}J_{F-Pt}$ = 589), −29.61 (dd, $^{3}J_{F-Pcis}$ = 8.3, $^{3}J_{F-Ptrans}$ = 55.1, $^{2}J_{F-Pt}$ = 584)	[b]
(diop)Pt(CF_3)Cl	302 m (ν_{Pt-Cl})	−23.69 (dd, $^{3}J_{F-Pcis}$ = 14.5, $^{3}J_{F-Ptrans}$ = 55.8, $^{2}J_{F-Pt}$ = 537)	0.58 (dq (trans CF_3), $^{3}J_{P-F}$ = 55.8, $^{2}J_{P-P}$ = 19.7, $^{1}J_{P-Pt}$ = 1747), 2.45 (dq (cis CF_3), $^{3}J_{P-F}$ = 14.5, $^{2}J_{P-P}$ = 19.7, $^{1}J_{P-Pt}$ = 3991)
(diop)Pt(CF_3)(OH)	3635 w (ν_{O-H}), 3625 w, 3602 w (ν_{O-H})[c]	−25.55 (dd, $^{3}J_{F-Pcis}$ = 8.2, $^{3}J_{F-Ptrans}$ = 53.9, $^{2}J_{F-Pt}$ = 577), −18.87 (dd, $^{3}J_{F-Pcis}$ = 14.4, $^{3}J_{F-Ptrans}$ = 55.5, $^{2}J_{F-Pt}$ = 730), −9.95 (t, $^{3}J_{F-P}$ = 17.6, $^{2}J_{F-Pt}$ = 664)	[b]

[a] IR: in cm^{-1} as Nujol mulls. NMR: in ppm, J in Hz; CD_2Cl_2 as solvent; references $CFCl_3$, H_3PO_4; d = doublet, t = triplet, q = quartet. [b] Extensive overlapping of signals. [c] CH_2Cl_2 solution.

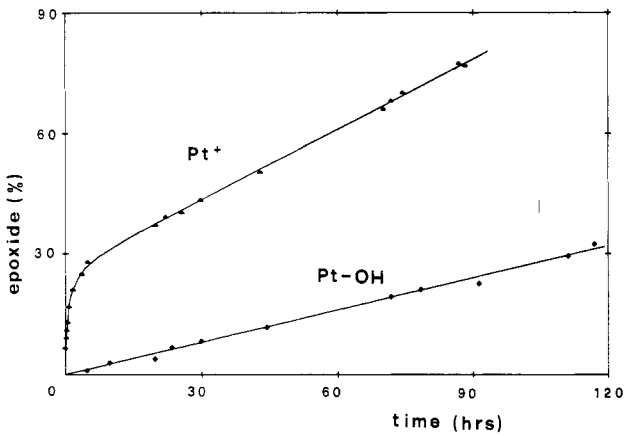


Figure 1. Reaction profiles for the catalytic epoxidation of 1-octene with H_2O_2 in the presence of [(chiraphos)Pt(CF_3)-(CH_2Cl_2)](BF_4) and (chiraphos)Pt(CF_3)(OH) at 0 °C.

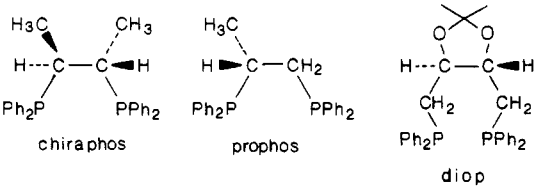
were obtained following the general procedure outlined in ref 22, which involves ligand exchange on *trans*-(PPh_3)$_2$Pt(CF_3)Cl, followed by chloride abstraction with Ag^+ and finally addition of OH^- (reactions 1–3).

$$\textit{trans}\text{-}(PPh_3)_2Pt(CF_3)Cl + P_2^* \rightarrow P_2^*Pt(CF_3)Cl + 2PPh_3 \quad (1)$$

$$P_2^*Pt(CF_3)Cl + AgBF_4 \rightarrow [P_2^*Pt(CF_3)(solv)](BF_4) + AgCl \quad (2)$$

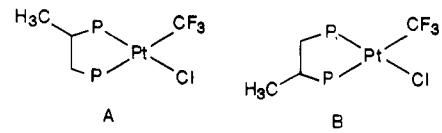
$$[P_2^*Pt(CF_3)(solv)](BF_4) + KOH \rightarrow P_2^*Pt(CF_3)(OH) + KBF_4 \quad (3)$$

The chiral diphosphines employed were (−)-2(*S*),3(*S*)-bis(diphenylphosphino)butane, (+)-2(*R*)-bis(diphenylphosphino)propane, and (+)-2,3-*o*-isopropylidene-2,3-dihydoxy-1,4-bis(diphenylphosphino)butane known as chiraphos, prophos, and diop, respectively.



The new chloro and hydroxo Pt(II) chiral complexes were characterized by IR and ^{19}F and $^{31}P\{^1H\}$ NMR spectroscopic measurements. Their typical spectroscopic features are reported in Table I. As shown, IR spectra reveal either typical Pt–Cl stretching modes in the 300–320 cm^{-1} region or weak bands around 3625 cm^{-1} characteristic[22] of the O–H stretching frequency for $P_2Pt(CF_3)(OH)$ complexes. As to the NMR data, only those relative to the chiraphos derivatives and (diop)Pt(CF_3)Cl are fully consistent with the proposed structures, while the others show more complicated patterns that deserve further comments.

The ^{19}F NMR spectrum of (prophos)Pt(CF_3)Cl shows two different CF_3 signals of equal intensity and close to each other (δ - 24.34 and −25.44), each of which is consistent with a square-planar cis-diphosphine platinum species. This behavior is paralleled in the IR spectrum by the existence of a double-tipped Pt–Cl band and is consistent with the existence of two structural isomers A and B, differing from the relative position of the CF_3 ligand



with respect to the methyl group of the diphosphine, which are statistically produced in equal amounts during the preparation procedure (reaction 1). Tentatively, we assign the higher field signal to A as a consequence of a shielding effect of the phenyl groups on the phosphorus cis, the rotations of which around the P–C bond are somehow restricted by the presence of the vicinal $-CH_3$ substituent.

The $^{31}P\{^1H\}$ NMR spectrum of (prophos)Pt(CF_3)Cl, which should consist of two sets of two doublets of quartets each with Pt satellites, is very difficult to analyze because of extensive overlapping of the individual signals.

(prophos)Pt(CF_3)(OH) shows (Table I) ^{19}F and $^{31}P\{^1H\}$ NMR behavior very similar to that reported for the corresponding chloride, again consistent with the existence of two structural isomers.

Finally the case of (diop)Pt(CF_3)(OH) is even more complicated as is clear from Table I. In fact, although microanalytical data (C, H) are in good agreement with the proposed formulation, the ^{19}F NMR spectrum reveals the presence of three different species: a major one (about 60% of the total) centered at δ −25.55 plus two minor

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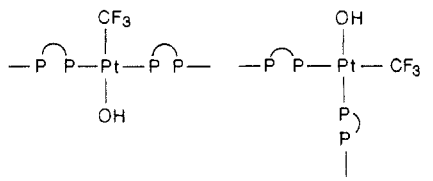
Table II. Catalytic Activity of the Chiral Pt(II) Complexes in the Epoxidation of Olefins[a]

catalyst	olefin	reactn temp, °C	initial rate, M s^{-1}	turnover 5 h	turnover 20 h	turnover 72 h
[(chiraphos)Pt(CF_3)(CH_2Cl_2)](BF_4)	1-octene	25	3.6×10^{-4}	31	54	90
[(chiraphos)Pt(CF_3)(CH_2Cl_2)](BF_4)	1-octene	0	2.1×10^{-4}	34	44	81
[(chiraphos)Pt(CF_3)(CH_2Cl_2)](BF_4)	propylene	0	4.1×10^{-4}	48	73	108
(chiraphos)Pt(CF_3)(OH)	1-octene	0	3.7×10^{-6}	0.7	4.0	23
[(prophos)Pt(CF_3)(CH_2Cl_2)](BF_4)	1-octene	25	2.5×10^{-4}	14	15	17
[(prophos)Pt(CF_3)(CH_2Cl_2)](BF_4)	1-octene	0	5.5×10^{-5}	18	21	32
[(prophos)Pt(CF_3)(CH_2Cl_2)](BF_4)	propylene	0	8.3×10^{-5}	20	26	27
(prophos)Pt(CF_3)(OH)	1-octene	0	6.7×10^{-6}	0.6	5.8	6.0
[(diop)Pt(CF_3)(CH_2Cl_2)](BF_4)	1-octene[b]	25	1.6×10^{-5}	2.4	2.6	2.8
[(diop)Pt(CF_3)(CH_2Cl_2)](BF_4)	1-octene[b]	0	1.6×10^{-5}	1.6	6.0	8.0
[(diop)Pt(CF_3)(CH_2Cl_2)](BF_4)	propylene	0	3.1×10^{-6}	1.4	2.1	3.5
(diop)Pt(CF_3)(OH)	1-octene	0	1.4×10^{-5}	0.2	0.2	0.3

[a] Experimental conditions: [Pt] = 2.0×10^{-2} M; [1-octene] = 2.4 M; propylene, 1 atm; H_2O_2/Pt 110, solvent CH_2Cl_2 (1-octene) or DCE (propylene). [b] 2-Octanone produced (<1%).

components of approximately equal intensity centered at δ −18.87 and −9.95, which show evidence for cis and trans geometries, respectively. While the major signal can be reasonably assigned to the monomeric, cis-diphosphine, hydroxo derivative, the two minor ones may arise from species of the type depicted.



It is in fact known[23] that coordinated diop can dissociate one of the phosphorus donors because of the less pronounced chelating character of the seven-membered ring. This view is supported by the further observation that when run in solution (CH_2Cl_2) the O–H stretching band appears to be resolved in two different components at 3625 and 3602 cm^{-1} (Table I).

Catalytic Epoxidation of Olefins. Propylene and 1-octene were chosen as prototype terminal olefins for the catalytic production of chiral epoxides with H_2O_2. Of these at least (*R*)-propylene oxide has found application as synthetic intermediate in the preparation of (*R*)-reciferolide.[24] The catalysts used were either [P_2*Pt(CF_3)(CH_2Cl_2)](BF_4) complexes or the corresponding P_2*Pt(CF_3)(OH). The reaction was tested at both 0 and 25 °C. Analogously to the homologous (diphenylphosphino)ethylene derivatives,[20,21] these catalysts display a very high chemoselectivity since epoxides are the only detectable oxidation products.

Typical reaction profiles of the epoxidation reaction are reported in Figure 1. As shown for the cationic complexes the conversion increases rapidly at the beginning of the reaction, but the system looses rapidly its initial activity. A summary of the catalysis results under the different experimental conditions is reported in Table II. Since the initial rates are not very representative of the overall capacity of the individual catalysts to produce epoxides, in Table II we report also the turnover numbers after 5, 20, and 72 h.

As a general trend the cationic catalysts are always more active than the corresponding hydroxo complexes, and this is consistent with the mechanism proposed[21] for this catalytic system. In fact we have previously shown that the generation of the active species proceeds through the following set of equilibria (ol = olefin):

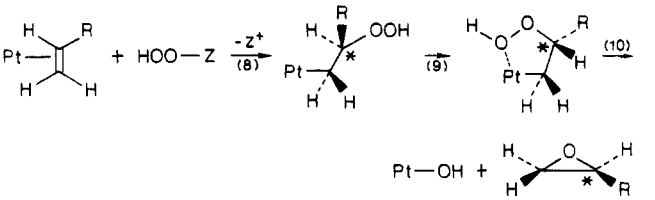
$$\text{Pt–OH} \rightleftharpoons \text{Pt}^+ + {}^-\text{OH} \quad (4)$$

$${}^-\text{OH} + \text{H}_2\text{O}_2 \rightleftharpoons {}^-\text{OOH} + \text{H}_2\text{O} \quad (5)$$

$$\text{Pt}^+ + {}^-\text{OOH} \rightleftharpoons \text{Pt–OOH} \quad (6)$$

$$\text{Pt}^+ + \text{ol} \rightleftharpoons \text{Pt(Ol)}^+ \quad (7)$$

Of course, when starting from cationic complexes the sequence is limited only to reaction 7 and results in a higher concentration of metal–olefin intermediate. Epoxide formation results from external nucleophilic attack of a hydroperoxidic oxidant on the coordinated olefin to produce a metal alkylhydroperoxide that can exist in two different configurations: open chain and cyclic (quasi-peroxymetallacycle), the latter giving the epoxide (eq 8–10). When the open-chain configuration is preferred



Z = H, Pt

(because of steric crowding around the axial position), the system produces ketones,[25] probably via β-hydride abstraction.[21] This view is supported by the results of Table II where it appears that the chiraphos and prophos derivatives are always more active than the corresponding diop derivatives. Indeed the lower efficiency of the diop derivatives with respect to the other catalysts is even more evident on a long time range, so that the system practically stops after 72 h and even after 2 weeks the amount of epoxide produced is so small that the separation of the products from the reaction mixture is practically impossible.

In one experiment the metal catalyst was separated from the reaction mixture at the end of the catalytic reaction by addition of Et_2O. IR analysis revealed that the complex was virtually pure [(diop)Pt(CF_3)(CH_2Cl_2)](BF_4), indicating that no decomposition had occurred. Moreover titration of the residual H_2O_2 showed no loss of active

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Table III. Optical Activity in the Catalytic Epoxidation of Terminal Olefins[a]

catalyst	epoxide	temp, °C	$[\alpha]^{21}_D$	ee, %
[(chiraphos)Pt(CF_3)(CH_2Cl_2)](BF_4)	1,2-epoxyoctane	25	−4.5	31 (*S*)
[(chiraphos)Pt(CF_3)(CH_2Cl_2)](BF_4)	1,2-epoxyoctane	0	−5.2	36 (*S*)
[(chiraphos)Pt(CF_3)(CH_2Cl_2)](BF_4)	1,2-epoxypropane	0	−6.1	41 (*S*)
(chiraphos)Pt(CF_3)(OH)	1,2-epoxyoctane	0	−2.6	18 (*S*)
[(prophos)Pt(CF_3)(CH_2Cl_2)](BF_4)	1,2-epoxyoctane	25	+4.1	28 (*R*)
[(prophos)Pt(CF_3)(CH_2Cl_2)](BF_4)	1,2-epoxyoctane	0	+4.0	28 (*R*)
[(prophos)Pt(CF_3)(CH_2Cl_2)](BF_4)	1,2-epoxypropane	0	+5.2	35 (*R*)
(prophos)Pt(CF_3)(OH)	1,2-epoxyoctane	0	+3.3	23 (*R*)

[a] Experimental conditions as in Table II. The prevailing enantiomer is given in parentheses.

oxygen in side reactions. Therefore the deactivation of the diop system must be found on a different ground.

Although the crystal structure of [(NBD)(diop)Rh](BPh_4) has shown[26] that with respect to the square plane of the complex the seven-membered ring and the ketal ring are approximately coplanar and projected away, it is obvious that in solution, due to the rotational flexibility of the seven-membered ring, many other stable conformations are possible, some of which can hinder strongly the axial position of the complex, as indicated by molecular models. In fact it is significant that in some cases with diop derivatives small amounts of ketone are produced during the catalytic reaction (Table II). The idea of evaluating the steric crowding around the axial position to account for the catalytic activity of the complexes will be further supported when the chiraphos derivatives are compared with respect to the prophos derivatives (vide infra).

At the end of the individual reactions, the epoxides obtained were distilled in vacuo and their specific rotations were measured in order to evaluate the optical purity [lit. (*R*)-1,2-epoxypropane, $[\alpha]^{21}_D$ +15.0° (*c* 40 in Et_2O);[27] (*R*)-1,2-epoxyoctane, $[\alpha]^{21}_D$ +14.5° (*c* 3.6 in EtOH)[28]]. These are reported in Table III. Unfortunately with the diop derivatives the amounts of epoxides produced were too small to allow distillation. However, with the chiraphos and prophos complexes the ee's measured are the highest obtained with a traditional catalytic system. These are second only to those obtained with the microbiological system derived from *Pseudomonas oleovorans*,[13,29,30] where, however, optically active 1,2-epoxyoctane was produced by selective "digestion" of a racemic mixture (ee 70%)[30] and rival with the biomimetic systems described by Groves[14] and Mansuy,[15] both based on chiral iron–porphyrin complexes as catalysts and iodosylbenzene as the oxidant. In these latter cases the best results were reported for the epoxidation of *p*-chlorostyrene (ee 51%)[14] while in the case of 1-octene the enantiomeric purity was significantly lower (ee 20%).[14] No results were reported for propylene. However, our system shows better stability and ease of operation. All complexes are air-stable and can be recovered quantitatively at the end of the catalytic reaction: the PtOH complexes unaltered and the Pt^+ starting complexes as a mixture of Pt^+ and PtOH (IR evidence). Moreover, H_2O_2 is of superior practical use compared to the costly and highly toxical PhIO.

As it appears from Table III, the *S* enantiomer is always preferentially produced with the chiraphos complexes, while the *R* enantiomer is always preferred with the prophos complexes. A similar trend was found with rhodium-based catalysts in the enantioselective hydrogenation of α-(*N*-acylamino)acrylic acids,[31,32] although the absolute configuration of the products was inverted.

Induction of Asymmetry. In an attempt to evaluate the factors that determine the extent of asymmetric induction, first of all we will have to go back to the mechanism of the epoxidation reaction. We will focus on the only two reactions in the overall process leading to the so-called "diastereotopic interaction",[19] i.e. reaction 7, which constitutes the key step where discrimination between the two enantiotopic faces of the olefin occurs, and reaction 8, where the asymmetric carbon is actually generated.

We will first examine reaction 8, i.e. the external nucleophilic attack of the oxidant on the coordinated olefin. From this point of view this system bears close similarities to the Wacker process, where the external attack of nucleophile H_2O has been recognized to be stereospecific, yielding trans insertion products.[33,34] Moreover, in the case of platinum–diolefin complexes, this has been demonstrated several years ago by several authors[35] for a variety of nucleophiles (although not including water). Hence if we assume that the same behavior applies to the present system, we should conclude that reaction 8 does not affect the system discriminating ability, the origin of which would be sought in reaction 7 only. It has to be pointed out that the nature of the nucleophile in the present system differs significantly depending on the starting complex (Pt^+ or Pt–OH). Detailed kinetic studies[36] have shown that when starting with $P_2Pt(CF_3)(OH)$ complexes the oxidant (reaction 8) is indeed the Pt–OOH complex formed in situ by reaction with hydrogen peroxide. Conversely, when $[P_2Pt(CF_3)(solv)]^+$ is used, two independent oxidants are operative in reaction 8: H_2O_2 and the Pt–OOH complex. While the attack of H_2O_2 on the coordinate olefin can be reasonably assumed to be stereospecific (by analogy with H_2O), the same assumption is doubtful in the case of Pt–OOH, as it appears from Table III where a loss of asymmetric induction is evident when the cationic catalysts are compared to the corresponding hydroxo.

We will now go back to reaction 7 where most of the discriminating ability of the system resides, and we will

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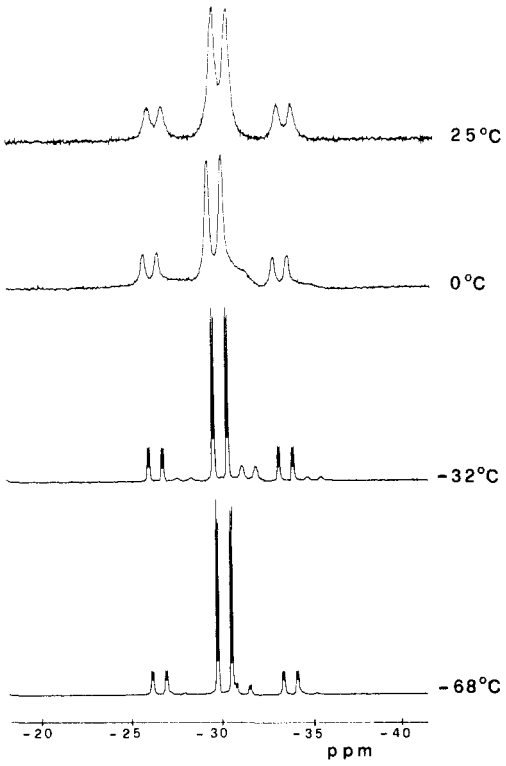


Figure 2. Variable-temperature ^{19}F NMR experiment carried out on [(chiraphos)Pt(CF_3)(CH_2Cl_2)](BF_4) in CD_2Cl_2.

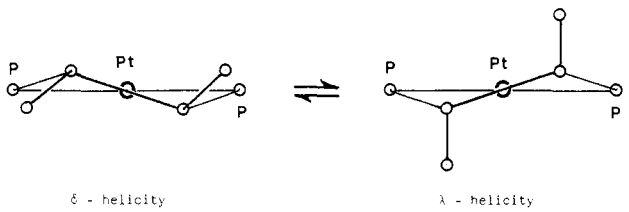


Figure 3. View of the five-membered chelate ring along the plane of the complex, in square-planar chiraphos–platinum derivatives showing the two conformers arising from different ring helicity.

try to explain the systematic capacity of the chiraphos derivatives to yield better ee's on the basis of simple considerations on the stereochemical rigidity of the chiraphos and prophos systems.

We have carried out some variable-temperature ^{19}F NMR experiments on [(chiraphos)Pt(CF_3)(CH_2Cl_2)](BF_4). As shown in Figure 2 at 25 °C the spectrum is fluxional and the expected doublet of doublets seems to coalesce into two broad bands centered about δ −30.08. Lowering the temperature reveals the existence of two different species (integration indicates a 4/1 ratio at −32 °C) that are static at −68 °C: C (δ −30.18 (dd, $^3J_{F-Pcis}$ = 7.4, $^3J_{F-Ptrans}$ = 55.0, $^2J_{F-Pt}$ = 516 Hz) and D (δ −31.13 (dd, $^3J_{F-Pcis}$ = 7.5, $^3J_{F-Ptrans}$ = 54.4, $^2J_{F-Pt}$ = 516 Hz). We attribute this equilibrium to two interconverting isomers (Figure 3) that differ in the conformation of the five-membered ring, δ helicity and λ helicity, which require the two methyl groups of the (*S*,*S*)-chiraphos to fit in the equatorial and axial positions, respectively. The more intense ^{19}F NMR signal is assigned to the more thermodynamically favored equatorial isomer.[31]

The same kind of behavior was observed when an excess of 1-octene was added into the NMR tube (Figure 4): again two isomer platinum–olefin species were present, slightly fluxional at 25 °C and static at 0 °C. The signal are centered at δ −22.49 (dd, $^3J_{F-Pcis}$ = 14.7, $^3J_{F-Ptrans}$ = 56.7, $^2J_{F-Pt}$ = 502 Hz) and −24.47 (dd, $^3J_{F-Pcis}$ = 14.3, $^3J_{F-Ptrans}$ = 56.2, $^2J_{F-Pt}$ = 503 Hz) with an intensity ratio of ~2.5/1 at 0 °C.

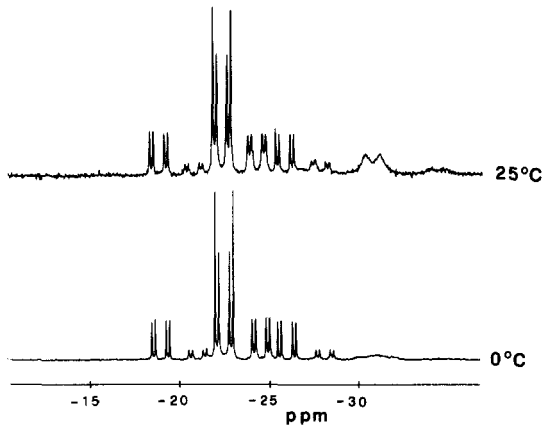
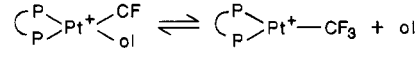


Figure 4. Variable-temperature ^{19}F NMR spectra of [(chiraphos)Pt(CF_3)(CH_2Cl_2)](BF_4) after addition of an excess of 1-octene.

This behavior was further confirmed when the same set of experiments was carried out on [(prophos)Pt(CF_3)(CH_2Cl_2)](BF_4). The spectrum of this compound that is very broad at 25 °C becomes static at −36 °C, where four different isomeric forms can be clearly distinguished. The signals are centered at δ −29.33 (dd, $^3J_{F-Pcis}$ = 8.8, $^3J_{F-Ptrans}$ = 55.3, $^2J_{F-Pt}$ = 515 Hz), −30.23 (dd, $^3J_{F-Pcis}$ = 7.7, $^3J_{F-Ptrans}$ = 55.5, $^2J_{F-Pt}$ = 512 Hz), −30.45 (dd, $^3J_{F-Pcis}$ = 8.6, $^3J_{F-Ptrans}$ = 56, $^2J_{F-Pt}$ = 516 Hz), and −31.52 (dd, $^3J_{F-Pcis}$ = 7.9,3$J_{F-Ptrans}$ = 55.5, $^2J_{F-Pt}$ = 516 Hz) of approximate intensity ratio 8/8/1/3, respectively at −36 °C. These four species are believed to be the conformational isomers (equatorial and axial) arising from the two structural isomers corresponding to A and B according to the equilibrium shown in Figure 3. Again the four-isomer spectrum is maintained on addition of excess of 1-octene. The spectrum is slightly fluxional at both 25 and 0 °C but static at −36 °C. The new signals are centered at δ −22.18 (dd, $^3J_{F-Pcis}$ = 15.2, $^3J_{F-Ptrans}$ = 56.5, $^2J_{F-Pt}$ = 509 Hz), −23.03 (dd, $^3J_{F-Pcis}$ = 14.0, $^3J_{F-Ptrans}$ = 57.3, $^2J_{F-Pt}$ = 500 Hz), −24.56 (dd, $^3J_{F-Pcis}$ = 12.9, $^3J_{F-Ptrans}$ = 56.3, $^2J_{F-Pt}$ = 561 Hz), and −25.59 (dd, $^3J_{F-Pcis}$ = 11.7, $^3J_{F-Ptrans}$ = 57.7, $^2J_{F-Pt}$ = 556 Hz) of approximate intensity ratio 1.8/1.2/1/2, respectively at −36 °C.

All these results were somehow unexpected since previous reports by Fryzuk and Bosnich[31,32] on chiraphos and prophos derivatives of Rh(I) and our above reported data on Pt–Cl and Pt–OH complexes seemed to grant the stereochemical rigidity of these systems in solution on the basis of the fact that the bulky equatorial methyl groups could not easily slide into the axial position. However, it is clear that when –Cl or –OH ligands are replaced with the more labile CH_2Cl_2 or olefin ligands, the square-planar complex may dissociate spontaneously (eq 10) to produce a transient three-coordinate intermediate with consequent widening of the P–Pt–P bond angle that will make the equatorial–axial equilibrium possible.



At any rate, an analysis of the ^{19}F NMR spectra of the Pt–olefin complexes at 0 and 25 °C (the temperatures at which the asymmetric epoxidations have been carried out) clearly shows that there is much more scrambling among the various conformational isomers in the case of prophos than in the case of chiraphos derivatives. This superior stereochemical rigidity of the chiraphos complexes with respect to prophos complexes is believed to be the main

reason to explain the systematically higher asymmetric induction observed with the former catalysts with respect to the latter. Moreover the higher steric hindrance around the axial position in the prophos derivatives is believed to be responsible of the lower catalytic activity of these systems (vide supra).

A further comparison with the work of Fryzuk and Bosnich[31,32] seems in order. As we have already pointed out, in our system the chiraphos derivatives produce preferentially *S* enantiomers, while the prophos derivatives produce *R* enantiomers. The contrary holds for the hydrogenation of α-(*N*-acylamino)acrylic acids catalyzed by Rh(I) complexes modified with the same chiral ligands. If we assume that in the epoxidation the external nucleophilic attack produces trans insertion products, while in the hydrogenation the internal hydride transfer produces cis insertion products,[37] the results observed in both cases are consistent with the same enantiotopic face of the olefin being preferentially coordinated by the two metal centers.

Conclusion. The chiral diphosphine approach to asymmetric epoxidation has proved useful, since it has enabled the achievement of the highest ee's so far obtained for a nonenzymatic or biologically related catalytic system. While the results obtained with the present platinum system do not compare with some spectacular asymmetric hydrogenations carried out with similarly modified rhodium complexes,[19] it has to be pointed out that, even with these latter systems, the >90% asymmetric inductions pertain *only* to functionalized olefins, where the "chelation" of the substrate on the metal center represents the major driving force leading to the high discrimination in the diastereotopic interaction. In this paper we have tried to emphasize the fundamental importance of the stereochemical rigidity of the catalyst molecular array in the absence of secondary interactions, and we have been able to show how the extent of this rigidity reflects on the final asymmetric induction. Further effort in this direction will probably lead to more appealing results that might be of some interest for use in organic synthesis.

Experimental Section

Apparatus. IR spectra in Nujol mulls were taken on a Perkin-Elmer 683 spectrophotometer using CsI windows. ^{19}F and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian FT 80A spectrometer operating in the FT mode, using as external references $CFCl_3$ and 85% H_3PO_4, respectively. Negative chemical shifts are upfield from the reference. GLC measurements were taken on a Hewlett-Packard 5790A gas chromatograph equipped with a 3390 automatic integrator. Identification of products was made with GLC by comparison with authentic samples. Specific rotations were measured on a Perkin-Elmer 241 polarimeter using thermostated microcells (optical path = 10 cm).

Materials. Solvents were dried and purified according to standard methods. 1-Octene (Fluka) was purified by passing through neutral alumina, distilled, and stored under N_2 in the dark. Propylene (99.9% SIAD), hydrogen peroxide (35% Fluka), (*S,S*)-chiraphos, (*R*)-prophos, and (+)-diop (all from Strem) were commercial products and were used without purification.

The preparation of new complexes was performed under dry N_2 by using conventional Schlenk and syringe techniques, although all of them were found to be air stable once isolated.

Preparation of New Chiral Complexes. All complexes were prepared from *trans*-$(PPh_3)_2Pt(CF_3)Cl$ following the general procedure outlined in ref 20. All complexes gave satisfactory elemental analysis (Table IV).

(chiraphos)Pt(CF_3)Cl. chiraphos (1.00 g, 2.34 mmol) and *trans*-$(PPh_3)_2Pt(CF_3)Cl$ (1.93 g, 2.34 mmol) were placed solid in a Schlenk flask, which was evacuated and filled with N_2. Dry, N_2-saturated toluene (50 mL) was added, and the suspension was stirred for 24 h at room temperature. The solvent was evacuated in vacuo to about half, and an equal amount of Et_2O was added to complete precipitation. The white solid was filtered, washed several times with Et_2O to eliminate traces of PPh_3, dried in vacuo, and recrystallized from CH_2Cl_2/Et_2O (yield 96%).

Table IV. Analytical Data of New Complexes

compd	anal. found (calcd) C	H
(chiraphos)Pt(CF_3)Cl	47.91 (47.99)	3.85 (3.89)
[(chiraphos)Pt(CF_3)(CH_2Cl_2)]BF_4	41.65 (41.80)	3.44 (3.51)
(chiraphos)Pt(CF_3)(OH)	49.31 (49.24)	4.10 (4.13)
(prophos)Pt(CF_3)Cl	47.18 (47.27)	3.71 (3.68)
[(prophos)Pt(CF_3)(CH_2Cl_2)]BF_4	40.92 (41.11)	3.26 (3.33)
(prophos)Pt(CF_3)(OH)	48.57 (48.49)	3.98 (3.92)
(diop)Pt(CF_3)Cl	48.13 (48.16)	3.99 (4.04)
[(diop)Pt(CF_3)(CH_2Cl_2)]BF_4	42.32 (42.47)	3.71 (3.67)
(diop)Pt(CF_3)(OH)	49.38 (49.30)	4.33 (4.27)

[(chiraphos)Pt(CF_3)(CH_2Cl_2)](BF_4). (chiraphos)Pt(CF_3)Cl (1.50 g, 2.23 mmol) was dissolved in dry, N_2-saturated CH_2Cl_2 (50 mL). To the solution was added 2.23 mL of a 1 M solution of $AgBF_4$ in acetone, and the mixture was stirred under N_2 for 2 h in the dark. AgCl was filtered off, and the resulting solution was centrifugated to eliminate traces of colloidal silver. The clear solution was brought to dryness in vacuo (10^{-2} torr) to yield a pale yellow solid (yield 98%).

(chiraphos)Pt(CF_3)(OH). [(chiraphos)Pt(CF_3)(CH_2Cl_2)](BF_4) (100 g, 1.16 mmol) was dissolved in dry, N_2-saturated acetone (50 mL). A 2.32-mL sample of a 1 M aqueous solution of KOH was added dropwise, followed by 2 mL of H_2O. The mixture was stirred for 2 h under N_2 and then evaporated to dryness in vacuo to yield an off-white solid. This was extracted with toluene (80 mL), and the residual solid was filtered off. The clear solution was evaporated in vacuo to a few milliliters, and the precipitation was completed by addition of Et_2O. The solid was filtered, washed with Et_2O, dried in vacuo, and recrystallized from CH_2Cl_2/Et_2O (yield 92%).

(prophos)Pt(CF_3)Cl. This complex was prepared following the same procedure as that for (chiraphos)Pt(CF_3)Cl, starting from prophos (1.00 g, 2.42 mmol) and *trans*-$(PPh_3)_2Pt(CF_3)Cl$ (1.99 g, 2.42 mmol). Since the complex is more soluble than the corresponding chiraphos derivative, a 1/1 toluene/heptane mixture (50 mL) was used instead of toluene. The product was recrystallized from CH_2Cl_2/Et_2O (yield 93%).

[(prophos)Pt(CF_3)(CH_2Cl_2)](BF_4). This complex was prepared as [(chiraphos)Pt(CF_3)(CH_2Cl_2)](BF_4), starting from (prophos)Pt(CF_3)Cl (1.50 g, 2.10 mmol) and $AgBF_4$ (2.10 mL, 1 M in acetone). Since the complex is more soluble than the corresponding chiraphos derivative, the amounts of solvents used were reduced (yield 98%).

(prophos)Pt(CF_3)(OH). The complex was prepared following the same procedures as that for (chiraphos)Pt(CF_3)(OH), starting from [(prophos)Pt(CF_3)(CH_2Cl_2)](BF_4) (1.00 g, 1.18 mmol) and KOH (2.36 mL, 1 M in H_2O). Since the complex is more soluble than the corresponding chiraphos derivative, the amounts of solvents used were reduced and the product was recrystallized from CH_2Cl_2/Et_2O (yield 90%).

(diop)Pt(CF_3)Cl. The complex was prepared as (prophos)-Pt(CF_3)Cl, starting from diop (1.00 g, 2.00 mmol) and *trans*-$(PPh_3)_2Pt(CF_3)Cl$ (1.65 g, 2.00 mmol) and recrystallized from CH_2Cl_2/Et_2O (yield 94%).

[(diop)Pt(CF_3)(CH_2Cl_2)](BF_4). This complex was prepared as [(prophos)Pt(CF_3)(CH_2Cl_2)](BF_4), starting from (diop)Pt-(CF_3)Cl (1.50 g, 1.89 mmol) and $AgBF_4$ (1.89 mL, 1 M in acetone) (yield 97%).

(diop)Pt(CF_3)(OH). This complex was prepared as (prophos)Pt(CF_3)(OH), starting from [(diop)Pt(CF_3)(CH_2Cl_2)](BF_4) (1.00 g, 1.07 mmol) and KOH (2.14 mL, 1 M in H_2O), and recrystallized from CH_2Cl_2/Et_2O (yield 88%).

Asymmetric Epoxidations. Reactions were carried out in a 25-mL round-bottomed reactor equipped with N_2 inlet and outlet. A side arm fitted with a silicone septum allowed sampling with a microsyringe during the course of the reaction. The system was kept at constant temperature (±0.1 °C) through an external

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jacket connected either to a thermostat (for 25 °C operations) or to a cryostat (for 0 °C operations). Stirring was performed by a Teflon-coated bar driven externally by a magnetic stirrer.

In a typical experiment the catalyst was charged in the reactor and the system was evacuated and filled with N_2. Then dry, N_2-saturated solvent (CH_2Cl_2) was introduced followed by 1-octene (final volume 8 mL). Finally H_2O_2 was injected through the silicone septum. The reaction mixture was periodically sampled, and the proceeding of the reaction was monitored with GLC. In the case of propylene, after addition of the solvent (DCE), the olefin was slowly flowed into the system for about 2 min and then maintained at constant pressure with the aid of a gas reservoir.

At the end of the reaction the organic phase was separated from the water phase, which was further extracted three times with small portions of organic solvent (CH_2Cl_2 or DCE). In the case of 1,2-epoxyoctane the organic phase was slowly evaporated to yield the crude product. This was distilled in vacuo to yield pure 1,2-epoxyoctane [bp 58–59 °C at 10 torr (lit.[38] bp 61 °C at 15 torr)]. Conversely, 1,2-epoxypropane was directly distilled from the organic phase at ambient pressure (bp 34 °C).

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Studies on the Transferability of Transition-Metal–Carbon and –Hydrogen Bond Enthalpies in Bis(cyclopentadienyl) Complexes

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New thermochemical studies involving the complexes $Ti(\eta^5\text{-}C_5H_5)_2(CH_3)_2$, $Ti(\eta^5\text{-}C_5H_5)_2(CH_3)Cl$, $Ti(\eta^5\text{-}C_5H_5)_2(C_6H_5)Cl$, and $W(\eta^5\text{-}C_5H_5)_2(H)I$ together with early data for the same type of molecules containing metal–carbon and metal–hydrogen bonds enabled a detailed discussion on the validity of transferring bond enthalpies. For this purpose, a method based on the bond enthalpy term concept, previously developed for complexes $M(\eta^5\text{-}C_5H_5)_2LL'$ (L = L'), was extended to molecules with L ≠ L'. This method also yields estimates of metal–ligand first bond dissociation enthalpies. The thermodynamics of the recently reported symmetrization reactions between $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ and $Ti(\eta^5\text{-}C_5H_5)_2R_2$ (R = CH_3, C_6H_5) is also described in the present study.

Introduction

The large number of recent papers and surveys on the energetics of transition-metal–carbon and –hydrogen σ-bonds reflects the importance of this subject in several areas of chemistry.[1-3] Gas-phase techniques are mainly responsible for the rapid growth of the metal–ligand bond energies data bank. These data shed light on the nature of those bonds and enabled us to establish correlations, which can be used to predict new values.[4] Most of the published gas-phase studies, however, deal with organometallic fragments and seldom with coordinatively saturated complexes, these being of greater importance for the preparative chemist. Equilibrium and kinetic studies in solution have been made by several groups to determine metal–carbon and –hydrogen bond enthalpy data in organometallic complexes,[2a-g,i] but the fact that it is not always simple to find a suitable reaction to apply those methods limits their use. This is one of the reasons why the calorimeter, in any of its several versions, is still widely applied to study the thermochemistry of transition-metal–organo complexes.[2h-l]

Calorimetric experiments usually yield an enthalpy of formation and rarely a metal–ligand bond dissociation enthalpy or even a difference between two of these quantities.[1a] If a complex has two or more types of ligands and one is interested in the energetics of a specific metal–ligand bond, then the knowledge of all the remaining bond enthalpies is necessary. These auxiliary data come, of course, from studies involving other molecules, which usually contain only one type of ligand.

The transferability of bond enthalpies is a central question in the area of organometallic thermochemistry. Recognizing when it is valid to identify bond enthalpies in different molecules will produce more reliable estimates of enthalpies of formation of molecules for which thermochemistry is either difficult or even impossible to study in the laboratory (e.g. transient species) and will therefore

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